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(54) **Cyclo-olefinic random copolymer composition and reaction product thereof**

Ungeordnete Cycloolefincopolymer-Zusammensetzung und deren Reaktionsprodukt

Composition d'un copolymère statistique de cyclo-oléfine et son produit de réaction

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(56) References cited:
EP-A- 0 018 751 **EP-A- 0 156 464**

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Description

This invention relates to a cyclo-olefinic random copolymer composition having excellent heat resistance, heat aging resistance, chemical resistance, weather resistance, solvent resistance, dielectric properties, rigidity, impact strength and moldability, and to a reaction product thereof.

Japanese Laid-Open Patent Publication No. 168708/1985 discloses a cyclo-olefinic random copolymer comprising ethylene and a specific cyclo-olefin component as a resin having excellent heat resistance, rigidity, weather resistance, transparency and dimensional accuracy during molding. This resin, however, does not necessarily have sufficient impact strength.

In an attempt to improve the impact strength of the above resin, a composition comprising the above resin and a rubber component is described in Japanese Laid-Open Patent publication No. 273655/88. The impact strength of this composition, however, is still insufficient, and a further improvement in impact strength is desired.

It is an object of this invention to provide a cyclo-olefinic random copolymer composition having excellent heat resistance, heat aging resistance, chemical resistance, weather resistance, solvent resistance, dielectric properties, rigidity, impact strength and moldability, and a reaction product thereof.

Accordingly the present invention provides a polymer composition comprising

(A) 100 parts by weight of a cyclo-olefinic random copolymer derived from ethylene and a cyclo-olefin and having an intrinsic viscosity [η], measured in decalin at 135°C, of 0.05 to 10 dl/g, a glass transition temperature (Tg) of 50 to 230°C, and a softening point of at least 70°C,
(B) 5 to 150 parts by weight of at least one flexible polymer having a glass transition temperature of not more than 0°C selected from

(a) a cyclo-olefinic random copolymer derived from ethylene, a cyclo-olefin and an alpha-olefin having 3 to 20 carbon atoms,
(b) an amorphous or low-crystalline olefinic copolymer derived from at least two components selected from ethylene and at least one alpha-olefin having 3 to 20 carbon atoms,
(c) an olefin/nonconjugated diene copolymer derived from a nonconjugated diene and at least two components selected from ethylene and at least one alpha-olefin having 3 to 20 carbon atoms, and
(d) an aromatic vinyl copolymer which is a random copolymer or block copolymer each derived from an aromatic vinyl hydrocarbon and a conjugated diene, and hydrogenation products of these copolymers, and

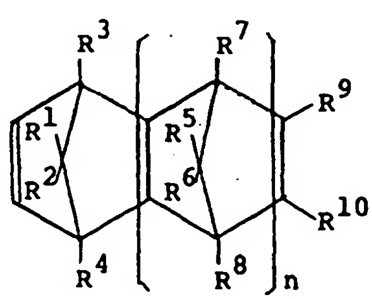
(C) 0.004 to 1.0 part by weight of an organic peroxide.

The present invention further provides a reaction product obtained by heat-treating a polymer composition as defined above under conditions which induce the decomposition of the organic peroxide (C).

The present invention also provides a process for preparing a reaction product which comprises heat-treating a polymer composition as defined above in the molten state at a temperature of 150 to 300°C for 10 seconds to 30 minutes or in a solution at a temperature of 50 to 300°C for 10 seconds to 2 hours to induce the decomposition of the organic peroxide (C).

The cyclo-olefinic random copolymer (A) used in the polymer composition of this invention comprises an ethylene component and a cyclo-olefin component. Cyclo-olefins of the following formulae (I) to (V) are especially preferably used:

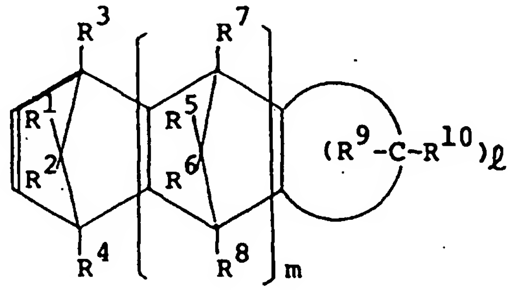
cyclo-olefin of formula (I)



.... (I)

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10}, which may be identical or different, each represents hydrogen, halogen or a monovalent hydrocarbon group, and n is 0 or a positive integer;

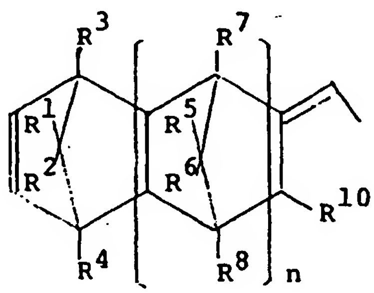
cyclo-olefins of formula (II)



.... (II)

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} are as defined in formula (I), m is 0 or a positive integer, and ℓ is an integer of at least 3;

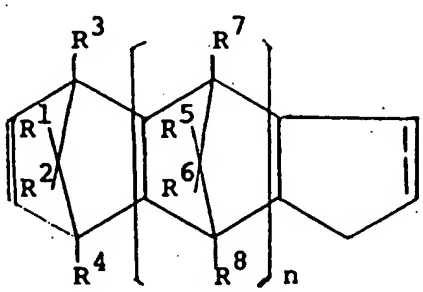
cyclo-olefins of formula (III)



.... (III)

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8 and R^{10} and n are as defined in formula (I);

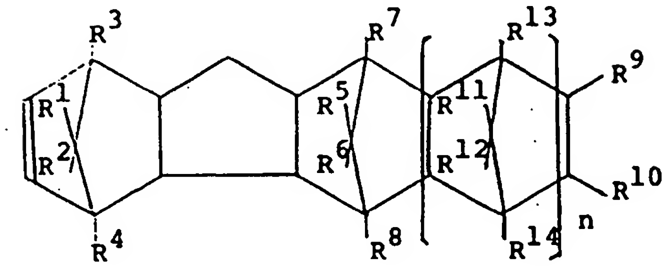
cyclo-olefins of formula (IV)



.... (IV)

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8 and n are as defined in formula (I); or

cyclo-olefins of formula (V)



.... (V)

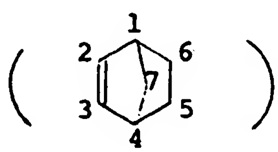
wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} an n are as defined in formula (I), and R^{11}, R^{12}, R^{13} and R^{14}, independently from each other and from R^1, each represents hydrogen, halogen or a monovalent hydrocarbon group.

The cyclo-olefins of formulae (I) and (II) are especially preferred. These cyclo-olefins may be used singly or in combination with one another.

In formulae (I) to (V), the monovalent hydrocarbon group defined for R^1 to R^{14} is preferably a linear or branched alkyl group having 1 to 10 carbon atoms.

Examples of the cyclo-olefins of formula (I) include

bicyclo[2.2.1]hept-2-ene



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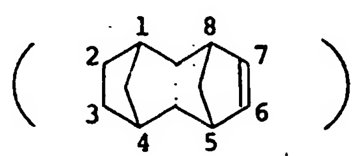
6-methylbicyclo[2.2,1]hept-2-ene,
5,6-dimethylbicyclo[2.2.1]hept-2-ene,
1-methylbicyclo[2.2.1]hept-2-ene,
6-ethylbicyclo[2.2.1]hept-2-ene,
6-n-butylbicyclo[2.2.1]hept-2-ene,
6-isobutyibicyclo[2.2,1]hept-2-ene,
7-methylbicyclo[2.2,1]hept-2-ene,
1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene



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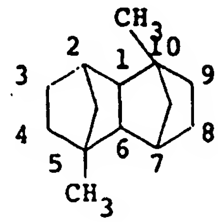
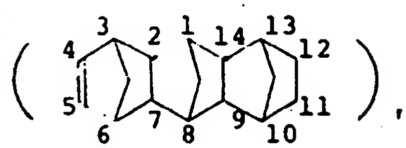
2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-propyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-hexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2,3-dimethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-methyl-3-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-chloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-bromo-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-fluoro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2,3-dichloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-cyclohexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,

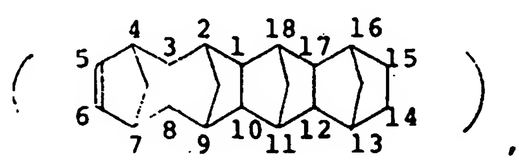
2-n-butyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-isobutyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8aoctahydronaphthalene,
5,10-dimethyltetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$]-3-dodecene



2,10-dimethyltetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$]-3-dodecene,
11,12-dimethyltetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$]-3-dodecene,
2,7,9-trimethyltetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$]-3-dodecene,
2,7,9-trimethyltetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$]-3-dodecene,
9-ethyl-2,7-dimethyltetracyclo[4.4.0.$1^{2,5}$.$1^{7,}$10]- 3-dodecene,
9-isobutyl-2,7-dimethyltetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$]-3-dodecene,
9,11,12-trimethyltetracyclo[4.4.0.$1^{2,5}$.$1^{7,}$10]-3-dodecene,
9-ethyl-11,12-dimethyltetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$]-3-dodecene,
9-isobutyl-11,12-dimethyltetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$]-3-dodecene,
5,8,9,10-tetramethyltetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$]-3-dodecene,
hexacyclo[6.6.1.$1^{3,6}$.$1^{10,13}$.$0^{2,7}$.$0^{9,14}$]-4-heptadecene



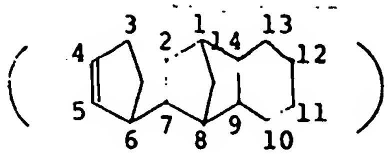
12-methylhexacyclo[6.6.1.$1^{3,6}$.$1^{10,13}$.$0^{2,7}$.$0^{9,14}$]-4-heptadecene,
12-ethylhexacyclo[6.6.1,$1^{3,6}$,$1^{10,13}$.$0^{2,7}$.$0^{9,14}$]4-heptadecene,
12-isobutylhexacyclo[6.6.1.1^{3},^{6}.$1^{10,13}$.$0^{2,7}$.$0^{9,-14}$]-4-heptadecene,
1,6,10-trimethyl-12-isobutylhexacyclo[6.6.1.$1^{3,6}$.$1^{10,13}$.$0^{2,7}$.$0^{9,14}$]-4-heptadecene,
octacyclo[8.8.0.$1^{2,9}$.$1^{4,7}$.$1^{11,18}$.$1^{13,16}$.$0^{3,8}$.$0^{12,17}$]-5-dococene



15-methyloctacyclo [8.8.0.$1^{2,9}$.$1^{4,7}$.$1^{11,18}$.$1^{13,16}$.$0^{3,8}$.$0^{12,17}$]5-dococene, and
15-ethyloctacyclo[8.8.0.$1^{2,9}$.$1^{4,7}$.$1^{11,18}$.$1^{13,16}$.$0^{3,8}$.$0^{12,17}$]-5-dococene.

Examples of the cycloolefins of general formula (II) include

pentacyclo[6.6.1.$1^{3,6}$.$0^{2,7}$.$0^{9,14}$]-4-hexadecene



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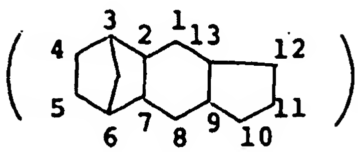
1,3-dimethylpentacyclo(6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]-4-hexadecene,
1,6-dimethylpentacyclo[6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]-4-hexadecene,
15,16-dimethylpentacyclo[6,6.1.13,6$_{0}$2,7$_{0}$9,14]4-hexadecene,
pentacyclo[6.5.1.1^{3,6}.0^{2,7}.0^{9,13}]-4-pentadecene,



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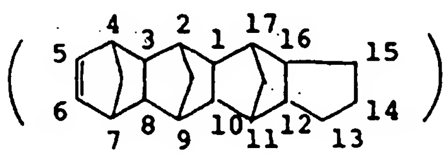
1,3-dimethylpentacyclo[6.5.1.1^{3,6}.0^{2,7}.0^{9,13}]-4-pentadecene,
1,6-dimethylpentacyclo[6.5.1.1^{3,6}.0^{2,7}.0^{9,13}]-4pentadecene,
14,15-dimethylpentacyclo[6.5.1.1^{3,6}.0^{2,7}.0^{9,13}]-4-pentadecene,
heptacyclo[8.7.0.1^{2,9}.1^{4,7}.1^{11,17}.0^{3,8}.0^{12,16}]-5-eicocene



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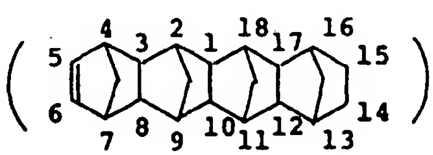
heptacyclo[8.8.0.1^{2,9}.1^{4,7}.1^{11,18}.0^{3,8}.0^{12,17}]-5-heneicocene,



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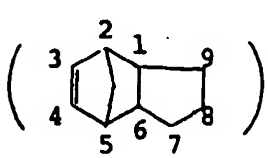
tricyclo[4.3.0.1^{2,5}]-3-decene



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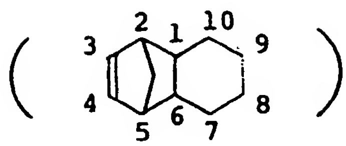
2-methyl-tricyclo[4.3.0.1^{2,5}]-3-decene,
5-methyl-tricyclo[4.3.0.1^{2,5}]-3-decene,
tricyclo[4.4.0.1^{2,5}]-3-undecene



10-methyl-tricyclo[4.4.0.$1^{2,5}$]-3-undecene.

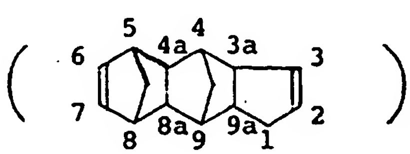
The cycloolefins of formulae (I) and (II) may easily be produced by condensing cyclopentadienes with the corresponding olefins by a Diels-Alder reaction.

Examples of the cyclo-olefins of formula (III) include

2-ethylidene-1,4,5,8-dimethano-1,2,3,4,4a,5,8,-8a-octahydronaphthalene,
2-ethylidene-3-methyl-1,4,5,8-dimethano-1,2,3,-4,4a,5,8,8a-octahydronaphthalene,
2-ethylidene-3-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-ethylidene-3-isopropyl-1,4,5,8-dimethano-1,2,-3,4,4a,5,8,8a-octahydronaphthalene,
2-ethylidene-3-butyl-1,4,5,8-dimethano-1,2,3,4,-4a,5,8,8a-octahydronaphthalene,
2-n-propylidene-1,4,5,8-dimethano-1,2,3,4,4a,5,-8,8a-octahydronaphthalene,
2-n-propylidene-3-methyl-1,4,5,8-dimethano-1,2,-3,4,4a,5,8,8a-octahydronaphthalene,
2-n-propylidene-3-ethyl-1,4,5,8-dimethano-1,2,-3,4,4a,5,8,8a-octahydronaphthalene,
2-n-propylidene-3-isopropyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-n-propylidene-1,4,5,8-3-butyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-isopropylidene-1,4,5,8-dimethano-1,2,3,4,4a,-5,8,8a-octahydronaphthalene,
2-isopropylidene-3-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
2-isopropylidene-3-ethyl-1,4,5,8-dimethano-1,2,-3,4,4a,5,8,8a-octahydronaphthalene,
2-isopropylidene-3-isopropyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, and
2-isopropylidene-3-butyl-1,4,5,8-dimethano-1,2,-3,4,4a,5,8,8a-octahydronaphthalene.

These compounds of formula (III) are described in Japanese Laid-Open Patent Publication No. 305111/1988, and can be easily produced by reacting cyclopentadiene compounds (or dicyclopentaidnes) with alkylidenebicyclo-[2.2.1] hept-2-ene compounds such as 5-ethylidenebicyclo[2,2,1]hept-2-enes by a Diels-Alder reaction.

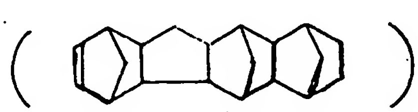
An example of the compound of formula (IV) is 4,9,5,8-dimethano-3a,4,4a,5,8,8a,9,9a-octahydro-1H-benzoindene of formula



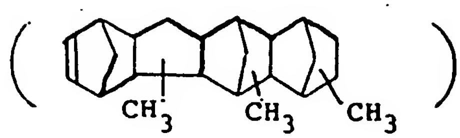
The compounds of formula (IV) are described in Japanese Laid-Open Patent Publication No. 243111/1988, and can be produced by a Diels-Alder reaction of di-cyclopentdienes and cyclopentadienes.

Examples of the cyclo-olefins of formula (V) include

heptacyclo[$1^{3,6}$.$1^{19,17}$.$1^{12,15}$.0.$0^{2,7}$.$0^{11,16}$]-icos-4-ene



trimethyl-heptacyclo[$1^{3,6}$.$1^{19,17}$.$1^{12,15}$.0.$0^{2,7}$..$0^{11,16}$]-icos-4-ene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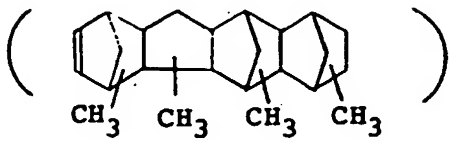
tetramethyl-heptacyclo[$1^{3,6}.1^{19,17}.1^{12,15}.0.0^{2,7}.-0^{11,16}$]-icos-4-ene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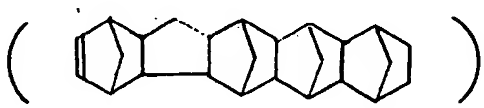
nonacyclo[$1^{1,11}.1^{15,0}.1^{13,20}.1^{15,18}.0^{2,10}.0^{4,9}.-0^{12,21}.0^{14,19}$]-pentacos-6-ene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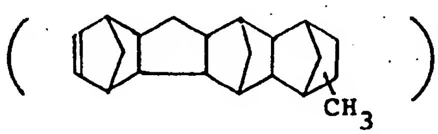
methyl-heptacyclo[$1^{3,6}.1^{19,17}.1^{12,15}.0.0^{2,7}.-0^{11,16}$]- icos-4-ene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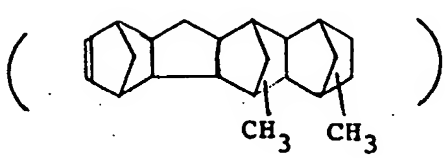
and
methyl-heptacyclo[[$1^{3,6}.1^{19,17}.1^{12,15}.0.0^{2,7}.-0^{11,16}$]-icos-4-ene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The cyclo-olefins of formula (V) are disclosed in WO89/01950, Laid-Open Specification (PCT/JP85/00849). They may be easily obtained by a Diels-Alder reaction of pentacyclo[6.5.$1^{1,7}.1^{9,12}.0^{2,6}.0^{8,13}$]-pentadec-3-enes (partially hydrogenated products of tricyclopentadienes) and cyclopentadienes.

The cyclo-olefinic random copolymer (A) used in the present invention can be produced by copolymerizing ethylene with at least one of the cyclo-olefins described above. The production method is disclosed, for example, in U. S. Patent No. 4,614,778. As required, another copolymerizable unsaturated monomer may be used in combination in the copolymerization. Examples of the other unsaturated monomer are alpha-olefins having 3 to 20 carbon atoms such as propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene and cycloolefins and cycloodienes such as norbornene, ethylidene norbornene and cyclopentadiene.

The cyclo-olefinic random copolymer (A) used in this invention preferably is composed of 40 to 85 mole %, particularly 50 to 75 mole %, of ethylene units and 15 to 60 mole %, particularly 25 to 50 mole %, of cyclo-olefin units based on the total of the ethylene and cyclo-olefin units. The proportion of the other olefin component if used should be smaller than that of the ethylene component.

The cyclo-olefinic random copolymer (A) has an intrinsic viscosity [η], measured in decalin at 135 °C, of 0.05 to 10 dl/g, preferably 0.08 to 5 dl/g. The cyclo-olefinic random copolymer is substantially linear, and does not contain a gel-like crosslinked structure. This can be substantiated by the fact that it completely dissolves in decalin at 135 °C.

The cyclo-olefinic random copolymer (A) has a softening point measured by a thermomechanical analyzer (TMA) of at least 70 °C, preferably 90 to 250 °C, particularly preferably 100 to 200 °C, and a glass transition temperature (Tg) of 50 to 230 °C, preferably 70 to 210 °C.

Furthermore, the cyclo-olefinic random copolymer (A) used in this invention generally has a crystallinity, measured by X-ray diffractometry, of 0 to 10 %, preferably 0 to 7 %, especially preferably 0 to 5 %.

The flexible polymer constituting component (B) is selected from the groups (a),(b),(c) and (d) as defined above. As a common characteristic, these flexible polymers have a glass transition temperature of not more than 0°C. The individual flexible polymers will be described below in detail.

The cyclo-olefin random copolymer (a) comprises an ethylene component, a cyclo-olefin component and an alpha-olefin component having 3 to 20 carbon atoms. Examples of the cyclo-olefin component may be the same as described hereinabove with regard to the copolymer (A). The cyclo-olefin component may be one or a combination of the cycloolefins, and the alpha-olefin component may be one or a combination of the alpha-olefins.

The cyclo-olefinic random copolymer (a) preferably comprises 40 to 98 mole % of ethylene units, 2 to 20 mole % of units of the cyclo-olefin, and 2 to 50 mole % of units of the alpha-olefin having 3 to 20 carbon atoms based on the total of the ethylene units, cyclo-olefin units and alpha-olefin units. Especially preferably, the copolymer (a) comprises 50 to 90 mole % of the ethylene units, 2 to 15 mole % of units of the cyclo-olefin and 5 to 40 mole % of units of the alpha-olefin component having 3 to 20 carbon atoms.

Preferably, the cyclo-olefinic random copolymer (A) is substantially linear with the above components arranged randomly.

The cyclo-olefinic random copolymer (a) has an intrinsic viscosity [η], measured in decalin at 135 °C, of preferably 0.01 to 10 dl/g, especially preferably 0.08 to 7 dl/g.

The cyclo-olefinic random copolymer (A) and the cyclo-olefinic random copolymer (a) used in this invention can be produced, for example, by the methods disclosed in Japanese Laid-Open Patent Publications Nos. 168708/1985, 120816/1986, 115912/1986, 115916/1986, 271308/1986, 272216/1986, 252406/1987 and 252407/1987.

The amorphous or low-crystalline olefinic copolymer comprises at least two components selected from an ethylene component and alpha-olefin components having 3 to 20 carbon atoms. The alpha-olefins may be those exemplified hereinabove.

Preferably, the flexible olefinic copolymer (b) may be, for example, a copolymer of ethylene and an alpha-olefin having 3 to 20 carbon atoms or a copolymer of propylene and an alpha-olefin having 4 to 20 carbon atoms.

The alpha-olefin in the copolymer of the ethylene component and the alpha-olefin component (b) preferably has 3 to 10 carbon atoms.

The alpha-olefin in the copolymer (b) of propylene and the other alpha-olefin preferably has 4 to 10 carbon atoms.

Preferred examples of the copolymer are a copolymer comprising 50 to 95 mole %, preferably 30 to 95 mole %, of ethylene units and 50 to 5 mole %, preferably 70 to 5 mole %, of units of an alpha-olefin having 3 to 20 carbon atoms, based on the total weight, of these components and a copolymer comprising 30 to 95 mole %, preferably 50 to 95 mole %, of propylene units and 70 to 5 mole %, preferably 50 to 5 mole%, of units of an alpha-olefin having 4 to 20 carbon atoms based on the total weight of these components.

The olefin/nonconjugated diene copolymer (c) may preferably be, for example, a copolymer of ethylene, an alpha-olefin having 3 to 20 carbon atoms and a nonconjugated diene or a copolymer of propylene, an alpha-olefin having 4 to 20 carbon atoms, and a non-conjugated diene.

The alpha-olefin as one component of the copolymer may be the same as those exemplified above. Alpha-olefins having 3 to 10 carbon atoms are preferred among those having 3 to 20 carbon atoms, and alpha-olefins having 4 to 10 carbon atoms are preferred among those having 4 to 20 carbon atoms.

Examples of the nonconjugated diene are aliphatic non-conjugated dienes such as 1,4-hexadiene, 1,6-octadiene, 2-methyl-1,5-hexadiene, 6-methyl-1,5-heptadiene and 7-methyl-1,6-octadiene, cyclic non-conjugated dienes such as cyclohexadiene, dicyclopentadiene, methyltetrahydroindene, 5-vinylnorbornene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-isopropylidene-2-norbornene and 6-cloromehtyl-5-iso-propenyl-2-norbomene, 2,3-idiisopropylidene-5-norbornene, 2-ethylidene-3-isopropylidene-5-norbornene and 2-propenyl-2,2-norbornadiene.

The olefin/nonconjugated diene copolymer (c) is preferably a copolymer comprising 30 to 95 mole %, preferably 50 to 95 mole %, of ethylene units and 70 to 5 mole %, preferably 50 to 5 mole %, of units of an alpha-olefin having 3 to 20 carbon atoms based on the total of the ethylene units and units of the alpha-olefin and 1 to 20 mole %, preferably 2 to 15 mole %, of units of a non-conjugated diene based on the total of the ethylene units, units of the alpha-olefin and units of the nonconjugated diene, a copolymer comprising 50 to 95 mole % of propylene units and 50 to 5 mole % of units of an alpha-olefin having 4 to 20 carbon atoms based on the total of the ethylene units and units of the alpha-olefin, and 1 to 20 mole %, preferably 2 to 15 mole %, of units of a nonconjugated diene based on the total of the

propylene units, units of the alpha-olefin and units of the nonconjugated diene.

The aromatic vinyl copolymer (d) is a random or block copolymer each derived from an aromatic vinyl hydrocarbon and a conjugated diene, or a hydrogenation product of the copolymer. Styrene is a preferred example of the aromatic vinyl hydrocarbon.

Examples of preferred conjugated dienes include butadiene and isoprene.

Advantageously, a styrene/butadiene block copolymer rubber, a styrene/butadiene/styrene block copolymer rubber, a styrene/isoprene/block copolymer rubber, a styrene/isoprene/styrene block copolymer rubber, a hydrogenated styrene/butadiene/styrene block copolymer rubber, a hydrogenated styrene/isoprene/styrene block copolymer rubber and a styrene/butadiene random copolymer rubber, for example, may advantageously be used as the aromatic vinyl copolymer (d).

Preferably, the aromatic vinyl copolymer (d) is a copolymer comprising 10 to 70 mole % of units of an aromatic vinyl hydrocarbon and 90 to 30 mole % of units of a conjugated diene based on the total of units of the aromatic vinyl hydrocarbon and units of the conjugated diene, or a hydrogenation product thereof.

The above-exemplified hydrogenated styrene/butadiene/styrene block copolymer rubber is a copolymer rubber obtained by partially or wholly hydrogenating the double bonds remaining in a styrene/butadiene/styrene block copolymer rubber. The hydrogenated styrene/isoprene/styrene block copolymer rubber is a copolymer rubber obtained by partially or wholly hydrogenating the double bonds remaining in a styrene/isoprene/styrene block copolymer rubber.

As common properties, these flexible polymers (a), (b), (c) and (d) have a glass transition temperature of not more than 0 °C, preferably not more than -10 °C especially preferably not more than -20 °C, and an intrinsic viscosity [η], measured in decalin at 135 °C, of preferably 0.01 to 10 dl/g, especially preferably 0.08 to 7 dl/g.

For the purpose of this invention, the amorphous or low-crystalline nature of the polymer is expressed by its crystalinity, measured by X-ray diffractometry, of 0 to 10 %, preferably 0 to 7 %, especially preferably 0 to 5 %.

The flexible copolymers may be used singly or in combination with one another.

Another component of the polymer composition of this invention is an organic peroxide (C).

Examples of the organic peroxide (C) include ketone peroxides such as methyl ethyl ketone peroxide and cyclohexanone peroxide; peroxy ketals such as 1,1-bis(t-butylperoxy)cyclohexane and 2,2-bis(t-butylperoxy)octane; hydroperoxides such as t-butyl hydro peroxide, cumene hydroperoxide, 2,5-dimethylhexane-2,5-dihydroxyperoxide and 1,1,3,3-tetramethylbutyl hydro peroxide; dialkyl peroxides such as di-t-butyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane and 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3; diacyl peroxides such as lauryl peroxide and benzoyl peroxide; and peroxy esters such as t-butyl peroxyacetate, t-butyl peroxybenzoate and 2,5-dimethyl-2,5-di(benzoylperoxy) hexane.

The polymer composition of this invention comprises 100 parts by weight of the cyclo-olefinic random copolymer (A), 5 to 150 parts by weight of at least one flexible polymer (B), and 0.004 to 1.0 part by weight of the organic peroxide (C).

More specificlally, the polymer composition of this invention contains 5 to 150 parts by weight, preferably 5 to 100 parts by weight, especially preferably 10 to 80 parts by weight, of the flexible copolymer (B) per 100 parts by weight of the cyclo-olefinic random copolymer (A).

The amount of the component (C) incorporated is 0.004 to 1 part by weight, preferably 0.05 to 0.5 part by weight, per 100 parts by weight of component (A).

In addition to the cyclo-olefinic random copolymer (A), the flexible copolymer (B) and the organic peroxide (C), the polymer composition may further comprise a compound having at least two radical-polymerizable functional groups in the molecule as component (D).

The inclusion of component (D) is preferred because it gives a polymer reaction product having higher impact strength.

The compound (D) having at least two radical-polymerizable functional groups in the molecule is, for example, divinylbenzene, vinyl acrylate or vinyl methacrylate. The amount of the component (d) to be included is not more than 1 part by weight, preferably 0.1 to 0.5 part by weight, per 100 parts by weight of components (A) and (B) combined.

As required, the copolymer composition in accordance with this invention may comprise, in addition to these components (A), (B), (C) and (D), conventional additives such as heat stabilizers, weather stabilizers, antistatic agents, slip agents, antiblocking agents, antihaze agents, lubricants, dyes, pigments, natural oils, synthetic oils, waxes, and organic or inorganic fillers. The amounts of these additives are properly determined according to the purposes for which the additivees are used.

The stabilizers include, for example, phenolic antioxidants such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]methane, alkyl beta-(3,5-di-t-butyl-4-hydroxyphenyl)propionates and 2,2'-oxamidebis(ethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate; fatty acid metal salts such as zinc stearate, calcium stearate and calcium 12-hydroxystearate; and esters of fatty acids with polyhydric alcohols, such as glycerol monostearate, glycerol monolaurate, glycerol distearate, pentaerythritol distearate and pentaerythritol tristearatre. They may be incorporated either singly or in combination. For example, a combination of tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propi-

onate]methane, zinc stearate and glycerol monostearate may be used.

The organic or inorganic fillers may include, for example, silica, diatomaceous earth, alumina, titanium dioxide, magnesium oxide, pumice powder, pumice balloon, aluminium hydroxide, magnesium hydroxide, basic magnesium carbonate, dolomite, calcium sulfate, potassium titanate, barium sulfate, calcium sulfite, talc, clay, mica, asbestos, glass fibers, glass flakes, glass beads, calcium silicate, montmorillonite, bentonite, graphite, aluminium powder, molybdenum sulfide, boron fibers, silicon carbide fibers, polyethylene fibers, polypropylene fibers, polyester fibers and polyamide fibers.

The polymer composition of this invention may be prepared by known methods. For examples, the components may be mixed simultaneously, but is is also possible to mix components (A) and (B), and then mix the resulting mixture with component (C) or both components (C) and (D). The latter method is preferred. When the additives are to be included, they are preferably mixed with components (A) and (B).

Mixing of components (A) and (B) may be carried out by an extruder. Alternatively, components (A) and (B) are fully dissolved in suitable solvents, for example saturated hydrocarbons such as heptane, hexane, decane and cyclohexane, or aromatic hydroxarbons such as toluene, benzene or xylene, and the solutions are then mixed (solution blending method). It is also possible to synthesize components (A) and (B) in separate polymerization vessels, and the resulting polymers (A) and (B) are blended in another vessel. The resulting composition of comonents (A) and (B) are then mixed with component (C) or both components (C) and (D) to give the polymer composition of this invention.

When the polymer composition of this invention is heat-treated at a temperature at which the organic peroxide as component (C) is decomposed, a reaction product of the polymer composition results.

The above heat-treatment is carried out by exposing the polymer composition to a temperature at which the organic peroxide (C) is decomposed, or at a higher temperature, preferably a temperature at which the half life of the organic peroxide (C) is 1 minute, or a higher temperature.

This heat-treatment reaction may be performed in the molten state by using, for example, an extruder. Alternatively, the compositon is dissolved in a solvent, and the heat-treament is carried out in solution.

The heat-treatment conditions may vary depending upon the type of the organic peroxide used. For example, when the treatment is carried out in the molten state, a temperature of 150 to 300 °C, and a period of 10 seconds to 30 minutes may preferably be employed. In the case of the treatment in solution, a temperature of 50 to 300 °C and a period of 10 seconds to 2 hours may preferably be used.

This reaction treatment may also be effected simultaneously with the operation of mixing component (C) with the composition composed of components (A) and (B).

In the above heat-treatment, the organic peroxide (C) is decomposed and a radical reaction takes place to give a reaction product in which components (A) and (B) are partially crosslinked. When the radical-polymerizable compound (D) is present in the composition, crosslinking takes place more easily to give a reaction product having excellent strength.

The resulting reaction product of the polymer composition has a crosslinked structure, and therefore has excellent heat resistance, chemical resistance, solvent resistance, dielectric properties, rigidity, transparency, impact strength and moldability. It can be advantageously used in the applications in which conventional cyclo-olefinic random copolymer compositions are used.

Specifically, a reaction product of polymer compositions of the invention having a low molecular weight are useful as as synthetic waxes in candles, impregnating agents for match splints, paper treating agents, sizing agents, rubber antioxidants, cardboard water-proofing agents, retarders for chemical fertilizers, ceramic binders, electrical insulators for paper capacitors, electric wires and cables, neutron deceleration agents, textile finishing aids, water-repellent agents for building materials, coating protecting agents, gloss agents, thixotropy imparting agents, agents for imparting hardness to pencil and crayon cores, substrates for carbon ink, electrophotographic toners, lubricants for molding of synthetic resins, mold releasing agents, resin colorants, hot-melt adhesives and lubricating greases. Polymer compositions of the invention having high molecular weights are useful as water tanks of electrical irons, electronic oven parts, base boards for printied circuits, circuit base boards for high frequency waves, electrically conductive sheets or films, camera bodies, housings of various measuring devices and instruments, various exterior and interior finishing materials for automobiles, automotive part, films, sheets and helmets.

The polymer reaction product provided by this invention is molded by known methods. For example, it may be fabricated by extrusion, injection molding, blow molding, rotational molding, and foaming-molding by using a single-screw extruder, a vent-type exruder, a twin-screw extruder, a conical twin-screw extruder, a co-kneader, a plasticator, a mixtruder, a twin-screw conical screw extruder, a planetary screw extruder, a gear extruder or a screwless extruder.

Since the polymer composition of this invention comprises the cyclo-olefinic random copolymer (A), the flexible copolymer (B) and the organic peroxide (C), it can be crosslinked by radical reaction to give a reaction product having excellent heat resistance, heat aging resistance, chemical resistance, solvent resistance, dielectric properties, rigidity and impact strength, particularly impact strength at low temperatures.

The following Examples further illustrate the present invenion.

The various properties in this invention are measured and evaluated by the following methods.

(1) Melt flow index ($MRF_{260\,°C}$)

Measured at a temperature of 260 °C under a load of 2.16 kg in accordance with ASTM D1238.

(2) Preparation of a test sample

An injection-molding machine (model IS-35 supplied by Toshiba Machinery Co., Ltd.) and a mold for a test sample were used, and the composition was molded under the following molding conditions.

Cylinder temperature:	220 °C
Mold temperature:	60 °C
Injection pressure:	primary=1000 kg/cm^2 secondary=800 kg/cm^2
Injection speed (primary):	30 mm/sec.
Screw rotating speed:	150 rpm
Cycles:	Injection + pressure holding=7 sec. cooling=15 sec.

(3)Bending teste

Performed in accordance with ASTM D790

Test piece shape:	5 x 1/2 x 1/8 t inches
Span distance:	51 mm
Test speed:	20 mm/min.
Test temperature:	23 °C

(4) Izod impact test

Performed in accordance with ASTM D256

Test specimen shape:	5/2 x 1/2 x 1/8 t inches (notched)
Test temperature:	23 °C

(5) Heat distortion temperature (HDT)

Test specimen shape:	5 x 1/4 x 1/2 t inches
Load:	264 psi

(6) Softening temperature (TMA)

Measured by means of a Thermom chanical analyzer made by Du Pont by the heat distortion behaviour of a sheet having a thickness of 1 mm. Specificaly, a quartz needle was placed on the sheet and a load of 49 g was applied. The temperature was elevated at a speed of 5 °C/min. The temperature at which the needle penetrated the sheet to a depth of 0.635 mm was defined as the softening temperature.

(7) Glass transition temperature (Tg)

Measured at a temperature elevation rate of 10 °C/min. by using DSC-20 (supplied by SEIKO Electronics Industry Co., Ltd.).

EXAMPLE 1

Four kilograms of pellets of a random copolymer of ethylene and 1,4,5,6-dimethano-1,2,3,4,4a,5,8,8a-octahydronapthalene (abbreviated as DMON) having an ethylene content, measured by ^{13}C-NMR, of 62 mole %, an $MFR_{260\,°C}$ of 35 g/10 min. an intrinsic viscosity, measured in decalin at 135 °C, of 0.47 dl/g, a softening temperature (TMA) of 148 °C a Tg of 137 °C as component (A) and 1 kg of pellets of an ethylene-propylene random copolymer (ethylene content 80 mole %, Tg=54 °C, $MFR_{230\,°C}$=0.7 g/10 min., [η]=2.2 dl/g) as component (B) were fully mixed, and then melt-blended by a twin-screw extruder (PCM 45 supplied by Ikegai Tekko Co., Ltd.) at a cylinder temperature of 220 °C. The blend was then pelletized by a pelletizer. One gram of Perhexyne 25B (trademark) (a product of Nippon Oils and Fats Co., Ltd.,
chemical structure:

$$
\begin{array}{c}
\quad CH_3 \quad\quad CH_3 \quad\quad\quad CH_3 \quad\quad\quad CH_3 \\
CH_3-\overset{|}{\underset{|}{C}}-O-O-\overset{|}{\underset{|}{C}}-C-C\equiv C-\overset{|}{\underset{|}{C}}-C-O-O-\overset{|}{\underset{|}{C}}-CH_3 \\
\quad CH_3 \quad\quad CH_3 \quad\quad\quad CH_3 \quad\quad\quad CH_3
\end{array}
$$

as component (C) and 3 g of divinylbenzene as component (D) were added to 1 kg of the pellets composed of components (A) and (B), and they were fully mixed. The resulting mixture was reacted in the molten state by using the above twin-screw extruder (cylinder temperature 230 °C) and pelletized.

Test pieces were prepared by the above methods, and their properties were measured.

The results are shown in Table 1.

EXAMPLES 2 - 4

Example 1 was repeated except that the type or amount of component (C) was varied.

The results are shown in Table 1.

EXAMLES 5 - 9

Example 1 was repeated except that each of he polymers indicated in Table 2 was used instead of the ethylene/ propylene random copolymer as component (B).

The results are shown in Table 2.

Table 1

Example	Component (C) Type	Component (C) Amount (g)	Flexural modulus (kg/cm^2)	Flexural strength (kg/cm^2)	Izod impact strength (kg.cm/cm)	HDT (°C)	MFR (g/10min)
1	Perhexyne 25B (*1)	1	19500	630	20	120	8
2	Perhexyne 25B (*1)	3	19700	620	22	122	7
3	Percadox 14(*2)	3	19300	620	19	120	7
4	Perbutyl D (*3)	3	19600	630	18	120	8

Note
(*1): trademark for a product of Nippon Oils and Fats, Co., Ltd.
(*2): trademark for a product of Japan Kayaku Noury, Co., Ltd.
(*3): trademark for a product of Nippon Oils and Fats, Co., Ltd.

Table 2

Example	Component (B)				Flexural modulus	Flexural strength	Izod impact strength	HDT	MFR
	Type	Composition	[η](dl/g)	Tg(°C)	(kg/cm²)	(kg/cm²)	(kg.cm/cm)	(°C)	(g/10min)
5	Ethylene/propylene random copolymer	Ethylene content 80 mole %	1.3	-55	19000	620	19	121	10
6	Ethylene/propylene ethylidene-norbornane random copolymer	Ethylene content 67 mole % Ethylidene norborene content 3 mole %	2.2	-45	20300	680	16	121	9
7	Ethylene/propylene/DMON random copolymer	Ethylene content 66 mole % DMON content 3 mole %	2.5	-35	20800	690	15	120	10
8	Styrene/isoprene/styrene block copolymer, hydrogenated	Styrene content 30 wt. %	0.65	-58 90	19600	640	13	120	14
9	Styrene/butadiene random copolymer	Styrene content 24 wt. %	1,5	-57	19800	650	16	119	9

EXAMPLE 10

Example 1 was repeated except that an ethylene/DMON random copolymer having an ethylene content of 71 mole %, an MFR of 20 g/10 min., an intrinsic viscosity of 0.60 dl/g, a softenintg point (TMA) of 115 °C, and a Tg of 98 °C was used instead of the ethylene/DMON random coppolymer used in Example 1. The resulting composition had the following properties.

Flexural modulus:	17300 kg/cm^2
Flexural strength:	640 kg/cm^2
Izod impact strength:	60 kg-cm/cm
HDT:	90 °C
$MFR_{260\,°C}$:	7 g/10 mn.

COMPARATIVE EXAMPLE

Example 1 was repeated except that components (C) and (D) were not used.
The resulting compostion had the following properties.

Flexural modulus:	22000 kg/cm^2
Flexural strength:	790 kg/cm^2
Izod impact strength:	5 kg-cm/cm
HDT:	124 °C
$MFR_{260\,°C}$:	16.2 g/10 mn.

Claims

1. A polymer composition comprising

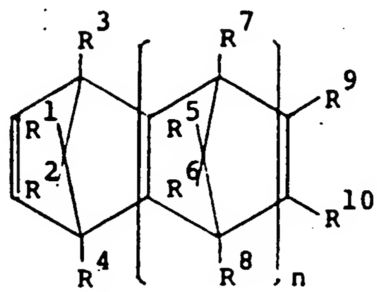
(A) 100 parts by weight of a cyclo-olefinic random copolymer derived from ethylene and a cyclo-olefin and having an intrinsic viscosity [η], measured in decalin at 135°C, of 0.05 to 10 dl/g, a glass transition temperature (Tg) of 50 to 230°C, and a softening point of at least 70°C,
(B) 5 to 150 parts by weight of at least one flexible polymer having a glass transition temperature of not more than 0°C selected from

(a) a cyclo-olefinic random copolymer derived from ethylene, a cyclo-olefin and an alpha-olefin having 3 to 20 carbon atoms,
(b) an amorphous or low-crystalline olefinic copolymer derived from at least two components selected from ethylene and at least one alpha-olefin having 3 to 20 carbon atoms,
(c) an olefin/nonconjugated diene copolymer derived from a nonconjugated diene and at least two components selected from ethylene and at least one alpha-olefin having 3 to 20 carbon atoms, and
(d) an aromatic vinyl copolymer which is a random copolymer or block copolymer each derived from an aromatic vinyl hydrocarbon and a conjugated diene, and hydrogenation products of these copolymers, and

(C) 0.004 to 1.0 part by weight of an organic peroxide.

2. A polymer composition according to claim 1 in which the cyclo-olefinic random copolymer (A) is derived from, as cyclo-olefin, at least one:

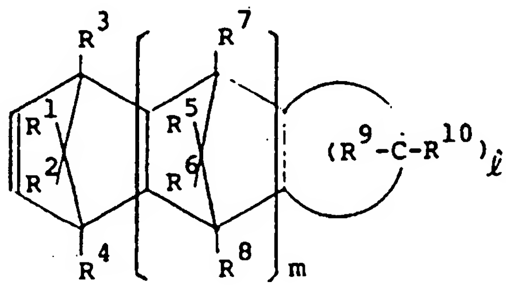
cyclo-olefin of formula (I)



.... (I)

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8 , R^9 and R^{10}, which may by the same or different, each represents hydrogen, halogen or a monovalent hydrocarbon group, and n is 0 or a positive integer;

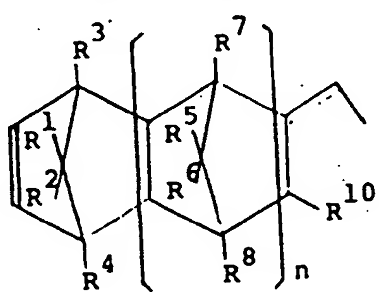
cyclo-olefin of formula (II)



.... (II)

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} are as defined in formula (I), m is 0 or a positive integer, and ℓ is an integer of at least 3;

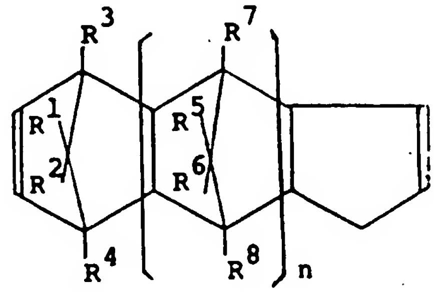
cyclo-olefin of formula (III)



.... (III)

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} and n are as defined in formula (I);

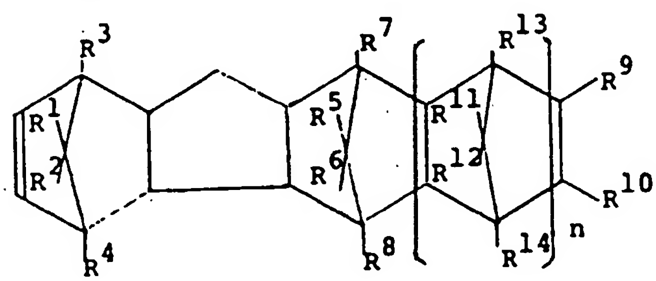
cyclo-olefin of formula (IV)



.... (IV)

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8 and n are as defined in formula (I); or

cyclo-olefin of formula (V)



.... (V)

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} and n are as defined in formula (I), and R^{11}, R^{12}, R^{13} and R^{14}, independently from each other and from R^1, each represents hydrogen, halogen or a monovalent hydrocarbon group.

3. A polymer composition according to claim 1 or 2 in which the cyclo-olefinic random copolymer (A) is composed of 40 to 85 mole % of ethylene units and 60 to 15 mole % of cyclo-olefin units based on the total of the ethylene and cyclo-olefin units.

4. A polymer composition according to claim 1, 2 or 3 in which the cyclo-olefinic random copolymer (A) has a crystallinity, measured by X-ray diffractometry, of 0 to 10%.

5. A polymer composition according to any one of claims 1 to 4 in which the flexible cycloolefinic random copolymer (B) (a) is derived from at least one cycloolefin of formulae (I), (II), (III), (IV) and (V) as defined in claim 2.

6. A polymer composition according to any one of the preceding claims in which the flexible cyclo-olefinic random copolymer (B) (a) comprises 40 to 98 mole% of ethylene units, 2 to 20 mole of units of the cyclo-olefin, and 2 to 50 mole% of units of the alpha-olefin based on the total of the ethylene units, cyclo-olefin units and alpha-olefin units.

7. A polymer composition according to any one of the preceding claims in which the flexible cyclo-olefinic random copolymer (B) (a) has an intrinsic viscosity [η], measured in decalin at 135°C, of 0.01 to 10 dl/g.

8. A polymer composition according to any one of claims 1 to 4 in which the flexible olefinic copolymer (B) (b) is a copolymer of ethylene with an alpha-olefin having 3 to 20 carbon atoms, or a copolymer of propylene with an alpha-olefin having 4 to 20 carbon atoms.

9. A polymer composition according to any one of claims 1 to 4 and 8 in which the flexible olefinic copolymer (B) (b) is a copolymer comprising 30 to 95 mole% of ethylene units and 70 to 5 mole% of units of an alpha-olefin having 3 to 20 carbon atoms based on the total of ethylene units and units of the alpha-olefin having 3 to 20 carbon atoms,

or a copolymer comprising 30 to 95 mole% of propylene units and 70 to 5 mole% of units of an alpha-olefin having 4 to 20 carbon atoms based on the total of propylene units and units of the alpha-olefin having 4 to 20 carbon atoms.

10. A polymer composition according to claim 9 in which the flexible olefinic copolymer (B) (b) is a copolymer comprising 50 to 95 mole% of ethylene units and 50 to 5 mole% of units of the alpha-olefin or a copolymer comprising 50 to 95 mole% of propylene units and 50 to 5 mole% of units of the alpha-olefin.

11. A polymer composition according to any one of claims 1 to 4 in which the flexible olefin/nonconjugated diene copolymer (B) (c) is a copolymer comprising 30 to 95 mole% of ethylene units and 70 to 5 mole% of units of an alpha-olefin having 3 to 20 carbon atoms based on the total of the ethylene units and units of the alpha-olefin and 1 to 20 mole% of units of a nonconjugated diene based on the total of the ethylene units, units of the alpha-olefin and units of the nonconjugated diene, or a copolymer comprising 50 to 95 mole% of propylene units and 50 to 5 mole% of units of an alpha-olefin having 4 to 20 carbon atoms based on the total of the propylene units and units of the alpha-olefin, and 1 to 20 mole% of units of a non-conjugated diene based on the total of the propylene units, units of the alpha-olefin and units of the nonconjugated diene.

12. A polymer composition according to any one of claims 1 to 4 in which the flexible aromatic vinyl copolymer (B) (d) comprises 10 to 70 mole% of units of an aromatic vinyl hydrocarbon and 90 to 30 mole% of units of a conjugated diene based on the total of units of the aromatic vinyl hydrocarbon and units of the conjugated diene, or a hydrogenation product thereof.

13. A polymer composition according to any one of the preceding claims which further comprises not more than 1 part by weight, per 100 parts by weight of the components (A) and (B), of (D) a compound having at least two radical-polymerizable functional groups in the molecule.

14. A reaction product obtained by heat-treating a polymer composition as claimed in any one of the preceding claims under conditions which induce the decomposition of the organic peroxide (C).

15. A process for preparing a reaction product which comprises heat-treating a polymer composition as claimed in any one of claims 1 to 13 in the molten state at a temperature of 150 to 300°C for 10 seconds to 30 minutes or in a solution at a temperature of 50 to 300°C for 10 seconds to 2 hours to induce the decomposition of the organic peroxide (C).

Patentansprüche

1. Polymermasse, umfassend

(A) 100 Gewichtsteile eines statistischen Cycloolefin-Copolymers, abgeleitet von Ethylen und einem Cycloolefin und mit einer Grundviskosität [η], gemessen in Decalin bei 135°C, von 0,05 bis 10 dl/g, einer Glasübergangstemperatur (Tg) von 50 bis 230°C und einem Erweichungspunkt von mindestens 70°C,

(B) 5 bis 150 Gewichtsteile mindestens eines flexiblen Polymers mit einer Glasübergangstemperatur von nicht mehr als 0°C, ausgewählt aus

(a) einem statistischen Cycloolefin-Copolymer, abgeleitet von Ethylen, einem Cycloolefin und einem α-Olefin mit 3 bis 20 Kohlenstoffatomen,

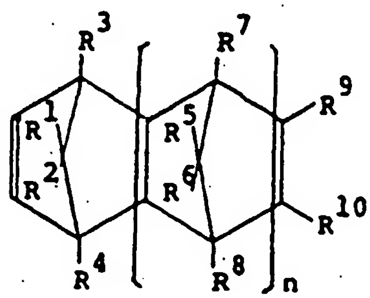
(b) einem amorphen oder gering-kristallinen Olefincopolymer, abgeleitet von mindestens zwei Komponenten, ausgewählt aus Ethylen und mindestens einem α-Olefin mit 3 bis 20 Kohlenstoffatomen,

(c) einem Olefin/nicht-konjugiertes-Dien-Copolymer, abgeleitet von einem nicht konjugierten Dien und mindestens zwei Komponenten, ausgewählt aus Ethylen und mindestens einem α-Olefin mit 3 bis 20 Kohlenstoffatomen, und

(d) einem aromatischen Vinylcopolymer, das ein statistisches Copolymer oder Blockcopolymer ist, jeweils abgeleitet von einem aromatischen Vinylkohlenwasserstoff und einem konjugierten Dien und Hydrierungsprodukten dieser Copolymere, und

(C) 0,004 bis 1,0 Gewichtsteile eines organischen Peroxids.

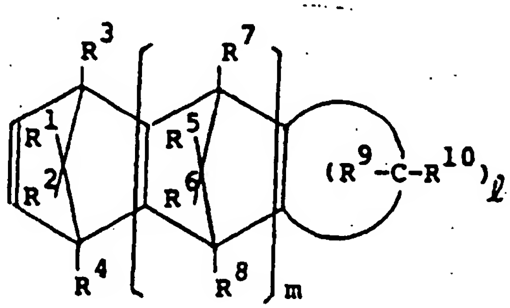
2. Polymermasse nach Anspruch 1, bei der das statistische Cycloolefin-Copolymer (A) abgeleitet ist von mindestens einem Cycloolefin der Formel (I)



.... (I)

in der R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 und R^{10}, die gleich oder verschieden sein können, jeweils Wasserstoff, Halogen oder eine einwertige Kohlenwasserstoffgruppe bedeuten und n 0 oder eine positive ganze Zahl ist,

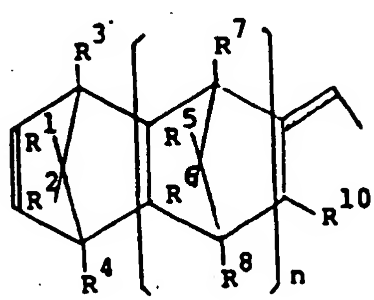
Cycloolefin der Formel (II)



.... (II)

in der R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 und R^{10} wie bei Formel (I) definiert sind, m 0 oder eine positive ganze Zahl ist und 1 eine ganze Zahl von mindestens 3 ist,

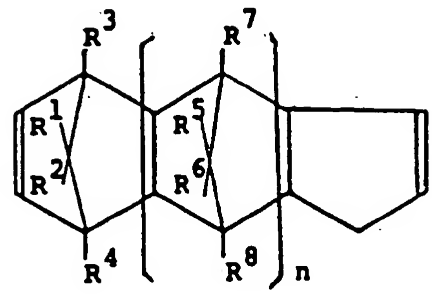
Cycloolefin der Formel (III)



.... (III)

in der R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 und R^{10} und n wie bei Formel (I) definiert sind;

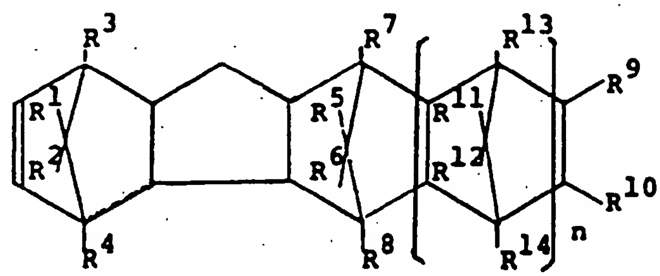
Cycloolefin der Formel (IV)



.... (IV)

in der R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8 und n, wie bei Formel (I) definiert sind, oder

Cycloolefin der Formel (V)



.... (V)

in der R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 und R^{10} und n wie bei Formel (I) definiert sind und R^{11}, R^{12}, R^{13} und R^{14} unabhängig voneinander und von R^1 jeweils Wasserstoff, Halogen oder eine einwertige Kohlenwasserstoffgruppe bedeuten,
als Cycloolefin.

3. Polymermasse nach Anspruch 1 oder 2, bei der das statistische Cycloolefin-Copolymer (A) aus 40 bis 85 Mol-% Ethyleneinheiten und 60 bis 15 Mol-% Cycloolefineinheiten, bezogen auf die Gesamtmenge der Ethylen- und Cycloolefineinheiten, besteht.

4. Polymermasse nach Anspruch 1, 2 oder 3, wobei das statistische Cycloolefin-Copolymer (A) eine Kristallinität, gemessen durch Röntgenbeugung, von 0 bis 10 % besitzt.

5. Polymermasse nach einem der Ansprüche 1 bis 4, wobei das flexible statistische Cycloolefin-Copolymer (B) (a) abgeleitet ist von mindestens einem Cycloolefin der Formeln (I), (II), (III), (IV) und (V), wie in Anspruch 2 definiert.

6. Polymermasse ach einem der vorangehenden Ansprüche, wobei das flexible statistische Cycloolefin Copolymer (B) (a), 40 bis 98 Mol-% Ethyleneinheiten, 2 bis 20 Mol-% Einheiten des Cycloolefins und 2 bis 50 Mol-% Einheiten des α-Olefins, bezogen auf die Gesamtmenge an den Ethyleneinheiten, Cycloolefineinheiten und α-Olefineinheiten, enthält.

7. Polymermasse nach einem der vorangehenden Ansprüche, wobei das flexible statistische Cycloolefin-Copolymer (B) (a) eine Grundviskosität [η] gemessen in Decalin bei 135°C von 0,01 bis 10 dl/g besitzt.

8. Polymermasse nach einem der Ansprüche 1 bis 4, wobei das flexible Olefincopolymer (B) (b) ein Copolymer von

Ethylen mit einem α-Olefin mit 3 bis 20 Kohlenstoffatomen oder ein Copolymer von Propylen mit einem α-Olefin mit 4 bis 20 Kohlenstoffatomen ist.

9. Polymermasse nach einem der Ansprüche 1 bis 4 und 8, wobei das flexible Olefincopolymer (B) (b) ein Copolymer ist, umfassend 30 bis 95 Mol-% Ethyleneinheiten und 70 bis 5 Mol-% Einheiten eines α-Olefins mit 3 bis 20 Kohlenstoffatomen, bezogen auf die Gesamtmenge an Ethyleneinheiten und Einheiten des α-Olefins mit 3 bis 20 Kohlenstoffatomen oder ein Copolymer, umfassend 30 bis 95 Mol-% Propyleneinheiten und 70 bis 5 Mol-% Einheiten eines α-Olefins mit 4 bis 20 Kohlenstoffatomen, bezogen auf die Gesamtmenge an Propyleneinheiten und Einheiten des α-Olefins mit 4 bis 20 Kohlenstoffatomen.

10. Polymermasse nach Anspruche 9, wobei das flexible Olefincopolymer (B) (b) ein Copolymer ist, umfassend 50 bis 95 Mol-% Ethyleneinheiten und 50 bis 5 Mol-% Einheiten des α-Olefins oder ein Copolymer, umfassend 50 bis 95 Mol-% Propyleneinheiten und 50 bis 5 Mol-% Einheiten des α-Olefins.

11. Polymermasse nach einem der Ansprüche 1 bis 4, wobei das flexible Olefin/nicht-konjugierte Dien-Copolymer (B) (c) ein Copolymer ist, umfassend 30 bis 95 Mol-% Ethyleneinheiten und 70 bis 5 Mol% Einheiten eines α-Olefins mit 3 bis 20 Kohlenstoffatomen, bezogen auf die Gesamtmenge der Ethyleneinheiten und Einheiten des α-Olefins und 1 bis 20 Mol-% Einheiten eines nicht-konjugierten Diens, bezogen auf die Gesamtmenge der Ethyleneinheiten, Einheiten des α-Olefins und Einheiten des nicht konjugierten Diens oder ein Copolymer, umfassend 50 bis 95 Mol-% Propyleneinheiten und 50 bis 5 Mol-% Einheiten eines α-Olefins mit 4 bis 20 Kohlenstoffatomen, bezogen auf die Gesamtmenge der Propyleneinheiten und Einheiten des α-Olefins und 1 bis 20 Mol-%-Einheiten eines nicht-konjugierten Diens, bezogen auf die Gesamtmenge der Propyleneinheiten, Einheiten des α-Olefins und Einheiten des nicht-konjugierten Diens.

12. Polymermasse nach einem der Ansprüche 1 bis 4, wobei das flexible aromatische Vinylcopolymer (B) (d) 10 bis 70 Mol-% Einheiten eines aromatischen Vinylkohlenwasserstoffs und 90 bis 30 Mol-% Einheiten eines konjugierten Diens, bezogen auf die Gesamtmenge an Einheiten des aromatischen Vinylkohlenwasserstoffs und Einheiten des konjugierten Diens, oder ein Hydrierungsprodukt davon umfaßt.

13. Polymermasse nach einem der vorangehenden Ansprüche, die zusätzlich nicht mehr als 1 Gewichtsteil auf 100 Gewichtsteile des Komponenten (A) und (B) an (D) einer Verbindung mit mindestens zwei radikalisch polymerisierbaren funktionellen Gruppen im Molekül enthält.

14. Reaktionsprodukt, erhalten durch Wärmebehandlung einer Polymermasse nach einem der vorangehenden Ansprüche unter Bedingungen, die die Zersetzung des organischen Peroxids (C) einleiten.

15. Verfahren zur Herstellung eines Reaktionsproduktes, umfassend die Wärmebehandlung einer Polymermasse nach einem der Ansprüche 1 bis 13 in geschmolzener Form bei einer Temperatur von 150 bis 300°C während 10 Sekunden bis 30 Minuten oder in einer Lösung bei einer Temperatur von 50 bis 300°C während 10 Sekunden bis 2 Stunden, um die Zersetzung des organischen Peroxids (C) einzuleiten.

Revendications

1. Composition de polymères comprenant :

(A) 100 parties en poids d'un copolymère statistique cyclo-oléfinique qui est dérivé de l'éthylène et d'une cyclo-oléfine, et qui présente une viscosité intrinsèque [η], mesurée dans la décaline à 135° C, valant de 0,05 à 10 dl/g, une température de transition vitreuse (Tg) de 50 à 230° C, et un point de ramollissement d'au moins 70° C,
(B) de 5 à 150 parties en poids d'au moins un polymère flexible, qui présente une température de transition vitreuse ne dépassant pas 0° C, choisi parmi

(a) un copolymère statistique cyclo-oléfinique, qui est dérivé de l'éthylène, d'une cyclo-oléfine et d'une alpha-oléfine comportant de 3 à 20 atomes de carbone,
(b) un copolymère oléfinique amorphe ou faiblement cristallin, qui est dérivé d'au moins deux composants choisis parmi l'éthylène et au moins une alpha-oléfine comportant de 3 à 20 atomes de carbone,
(c) un copolymère oléfine/diène non-conjugué, qui est dérivé d'un diène non-conjugué et d'au moins deux

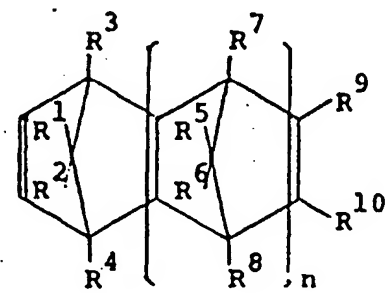
composants choisis parmi l'éthylène et au moins une alpha-oléfine comportant de 3 à 20 atomes de carbone, et

(d) un copolymère vinyl-aromatique, qui est un copolymère statistique ou un copolymère séquencé, chacun étant dérivé d'un hydrocarbure vinyl-aromatique et d'un diène conjugué, et des produits d'hydrogénation de ces copolymères, et

(C) de 0,004 à 1,0 partie en poids d'un peroxyde organique.

2. Composition de polymères conforme à la revendication 1, dans laquelle le copolymère statistique cyclo-oléfinique (A) est dérivé de, comme cyclo-oléfine, au moins :

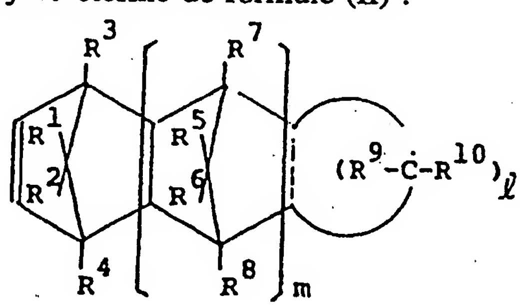
une cyclo-oléfine de formule (I) :



(I)

dans laquelle R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 et R^{10}, qui peuvent être identiques ou différents, représentent chacun un atome d'hydrogène, un atome d'halogène ou un groupe hydrocarboné monovalent, et n vaut 0 ou un nombre entier positif ;

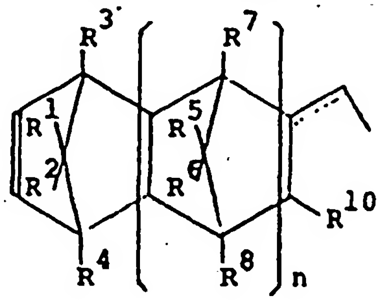
une cyclo-oléfine de formule (II) :



(II)

dans laquelle R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 et R^{10} sont tels que définis dans la formule (I), m vaut 0 ou un nombre entier positif, et 1 est un nombre entier valant au moins 3 ;

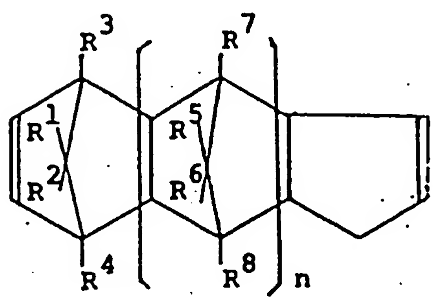
une cyclo-oléfine de formule (III) :



(III)

dans laquelle R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 et R^{10} et n sont tels que définis dans la formule (I) ;

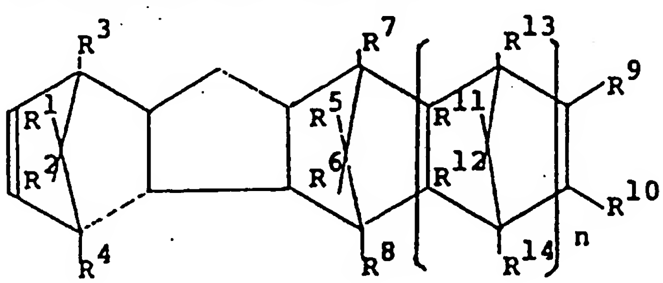
une cyclo-oléfine de formule (IV) :



(IV)

dans laquelle R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8 et n sont tels que définis dans la formule (I) ; ou

une cyclo-oléfine de formule (V) :



(V)

dans laquelle R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 et R^{10} et n sont tels que définis dans la formule (I), et R^{11}, R^{12}, R^{13} et R^{14}, indépendamment les uns des autres et de R^1, représentent chacun un atome d'hydrogène, un atome d'halogène ou un groupe hydrocarboné monovalent.

3. Composition de polymères conforme à la revendication 1 ou 2, dans laquelle le copolymère statistique cyclo-oléfinique (A) est composé de 40 à 85 % en moles de motifs éthylène et de 60 à 15 % en moles de motifs cyclo-oléfine, par rapport au total de motifs éthylène et de motifs cyclo-oléfine.

4. Composition de polymères conforme à la revendication 1, 2 ou 3, dans laquelle le copolymère statistique cyclo-oléfinique (A) a une cristallinité, mesurée par diffraction de rayons X, comprise entre 0 et 10 %.

5. Composition de polymères conforme à l'une quelconque des revendications 1 à 4, dans laquelle le copolymère

statistique cyclo-oléfinique flexible (B) (a) est dérivé d'au moins une cyclo-oléfine de formules (I), (II), (III), (IV) et (V) telles que définies dans la revendication 2.

6. Composition de polymères conforme à l'une quelconque des précédentes revendications, dans laquelle le copolymère statistique cyclo-oléfinique flexible (B) (a) comprend de 40 à 98 % en moles de motifs éthylène, de 2 à 20 % en moles de motifs cyclo-oléfine et de 2 à 50 % en moles de motifs alpha-oléfine, par rapport au total de motifs éthylène, de motifs cyclo-oléfine et de motifs alpha-oléfine.

7. Composition de polymères conforme à l'une quelconque des précédentes revendications, dans laquelle le copolymère statistique cyclo-oléfinique flexible (B) (a) a une viscosité intrinsèque [η], mesu-rée dans la décaline à 135° C, valant de 0,01 à 10 dl/g.

8. Composition de polymères conforme à l'une quelconque des revendications 1 à 4, dans laquelle le copolymère oléfinique flexible (B) (b) est un copolymère d'éthylène et d'une alpha-oléfine comportant de 3 à 20 atomes de carbone, ou un copolymère de propylène et d'une alpha-oléfine comportant de 4 à 20 atomes de carbone.

9. Composition de polymères conforme à l'une quelconque des revendications 1 à 4 et 8, dans laquelle le copolymère oléfinique flexible (B) (b) est un copolymère comprenant de 30 à 95 % en moles de motifs éthylène et de 70 à 5 % en moles de motifs alpha-oléfine comportant de 3 à 20 atomes de carbone, par rapport au total de motifs éthylène et de motifs alpha-oléfine comportant de 3 à 20 atomes de carbone, ou un copolymère comprenant de 30 à 95 % en moles de motifs propylène et de 70 à 5 % en moles de motifs alpha-oléfine comportant de 4 à 20 atomes de carbone, par rapport au total de motifs propylène et de motifs alpha-oléfine comportant de 4 à 20 atomes de carbone.

10. Composition de polymères conforme à la revendication 9, dans laquelle le copolymère oléfinique flexible (B) (b) est un copolymère comprenant de 50 à 95 % en moles de motifs éthylène et de 50 à 5 % en moles de motifs alpha-oléfine ou un copolymère comprenant de 50 à 95 % en moles de motifs propylène et de 50 à 5 % en moles de motifs alpha-oléfine.

11. Composition de polymères conforme à l'une quelconque des revendications 1 à 4, dans laquelle le copolymère oléfine/diène non-conjugué flexible (B) (c) est un copolymère comprenant de 30 à 95 % en moles de motifs éthylène et de 70 à 5% en moles de motifs alpha-oléfine comportant de 3 à 20 atomes de carbone, par rapport au total de motifs éthylène et de motifs alpha-oléfine, et de 1 à 20 % en moles de motifs diène non-conjugué, par rapport au total de motifs éthylène, de motifs alpha-oléfine et de motifs diène non-conjugué, ou un copolymère comprenant de 50 à 95 % en moles de motifs propylène et de 50 à 5 % en moles de motifs alpha-oléfine comportant de 4 à 20 atomes de carbone, par rapport au total de motifs éthylène et de motifs alpha-oléfine, et de 1 à 20 % en moles de motifs diène non-conjugué par rapport au total de motifs propylène, de motifs alpha-oléfine et de motifs diène non-conjugué

12. Composition de polymères conforme à l'une quelconque des revendications 1 à 4, dans laquelle le copolymère vinyl-aromatique flexible (B) (d) comprend de 10 à 70 % en moles de motifs hydrocarbonés vinyl-aromatiques et de 90 à 30 % en moles de motifs diène conjugué, par rapport au total de motifs hydrocarbonés vinyl-aromatiques et de motifs diène conjugué, ou un produit d'hydrogénation de ces derniers.

13. Composition de polymères conforme à l'une quelconque des précédentes revendications, qui comprend de plus une quantité ne dépassant pas 1 partie en poids, pour 100 parties en poids des composants (A) et (B), de (D) un composé ayant au moins deux groupes fonctionnels polymérisables sous forme radicalaire dans la molécule.

14. Produit réactionnel obtenu par traitement thermique d'une composition de polymères conforme à l'une quelconque des précédentes revendications dans des conditions qui provoquent la décomposition du peroxyde organique (C).

15. Procédé qui consiste à préparer un produit réactionnel qui comprend un traitement thermique d'une composition de polymères conforme à l'une quelconque des revendications 1 à 13 à l'état fondu à une température de 150 à 300° C pendant 10 s à 30 minutes ou, dans une solution à une température de 50 à 300° C pendant 10 s à 2 heures pour provoquer la décomposition du peroxyde organique (C).